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Effect of membrane hydrophilization on ultrafiltration performance for biomolecules separation

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ABSTRACT

This paper compares the performance of different hydrophilization methods to prepare low fouling ultrafiltration (UF) membranes. The methods include post-modification with hydrophilic polymer and blending of hydrophilic agent during either conventional or reactive phase separation (PS). The post-modification was done by photograft copolymerization of water-soluble monomer, poly(ethylene glycol) methacrylate (PEGMA), onto a commercial polyethersulfone (PES) UF membrane. Hydrophilization via blend polymer membrane with hydrophilic additive was performed using non-solvent induced phase separation (NIPS). In reactive PS method, the cast membrane was UV-irradiated before coagulation. The resulting membrane characteristic, the performance and hydrophilization stability were systematically compared. The investigated membrane characteristics include surface hydrophilicity (by contact angle /CA/), surface chemistry (by FTIR spectroscopy), and surface morphology (by scanning electron microscopy). The membrane performance was examined by investigation of adsorptive fouling and ultrafiltration using solution of protein or polysaccharide or humic acid. The results suggest that all methods could increase the hydrophilicity of the membrane yielding less fouling. Post-modification decreased CA from 44.8 ± 4.2^{o} to 37.8 ± 4.2^{o} to 42.5 ± 4.3^{o} depending on the degree of grafting (DG). The hydrophilization via polymer blend decreased CA from from 65^{o} to 54^{o} for PEG concentration of 5%. Nevertheless, decreasing hydraulic permeability was observed after post-modification as well as during polymer blend modification. Stability examination showed that there was leaching out of modifier agent from the membrane matrix prepared via conventional PS after 10 days soaking in both water and NaOH. Reactive PS could increase the stability of the modifier agent in membrane matrix.

1. Introduction

Biomolecules separation is an important process in many biological, medical and chemical industries. Many methods have been developed for the separation of biomolecules from their mixture including liquid chromatography, electrophoretic separation and membrane based processes. Its ability to separate macromolecular component, bacteria, viruses, cysts and other fine (bio)macromolecules, ultrafiltration (UF) has become an alternative promising separation process for biomolecules separations [1–5]. However, fouling, which causes significant loss of performance with respect to flux and often selectivity due to the deposition of suspended or dissolved on external surfaces, at the pore openings or within the membrane pores, is a severe problem during UF applications.

Since fouling significantly worsens UF membrane performance, efforts to overcome this problem have drawn more and more attention in the membrane research and application. In principle those efforts include feed pretreatment, advanced membrane and module design manufacturing, and process condition optimization. Previous works can be summarized as follows [1,6–8]: feed pretreatments and process conditions have been remarkably engineered to achieve better control of membrane fouling, but in most of the cases, the permeate fluxes are determined by the membrane itself.

As their mechanical strength, thermal and chemical stabilities as well as excellence film forming properties, PSf and PES are frequently used as material for UF membranes among the commercially available polymers [9]. Nevertheless, the hydrophobicity of those materials causes more significant fouling. Therefore, synthesis of low fouling polymeric UF membranes having good mechanical and chemical stability is very important from practical point of view.

Preparation of low fouling membrane for control of fouling is basically aimed to prevent/minimize undesired interactions (e.g., adsorption or adhesion process), because this will prevent or at least slow down the subsequent accumulation of colloids, e.g., denaturation and aggregation of protein [10]. In general, preparation of low fouling UF membranes can be done via two approaches, i.e. increasing membrane surface charge to promote electrostatic repulsion and

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hydrophilization to increase water—surface interaction [10]. In several applications, the charged membranes could dramatically reduce the fouling (e.g., [1,2,11]); however, the performance of low fouling membranes synthesized by this approach will strongly depend on the pH and ionic strength of the feed solution. In addition, this approach will be difficult to be practically applied for multi solutes/components in the feed solution. Hydrophilic membranes, on the other hand, have also shown low adsorptive as well as ultrafiltration fouling with protein (e.g., [7,12–14]). In some applications the charged membrane could have higher performance, but the performance of hydrophilic membrane should not be influenced by the physico-chemistry of the feed solution. Thus, this approach should be more flexible from practical applications.

To introduce hydrophilic modifier into polymeric membrane, three different approaches have been proposed, i.e., (i) membrane polymer modification (pre-modification), (ii) blending of the membrane polymer with modifying agent (additive), and (iii) surface modification after membrane preparation (post-modification) [15]. An important example for polymer modification before membrane formation (the first approach) is the sulfonation or carboxylation of PSf or PES [16]. Nevertheless, this approach can involve significant changes in composition of the casting or spinning solution, membrane structure formed during the phase separation. As consequent, the membrane properties can be quite different from the unmodified reference material. In addition, this approach is usually costly. Therefore, the second and third approaches are more realistic from practical application point of view. A lot of studies reported that UF membrane hydrophilization can be done via those two approaches [10,15]. Nevertheless, it is hard to determine the most excellent method based on previous studies. No specific study comparing both methods has been reported yet. In this paper, preparation of low fouling UF membranes via membrane surface modification (post-modification) and blending of membrane polymer with modifying agent are described and compared for biomolecules separation. In addition, integration of UV irradiation into phase separation method as a novel technique is proposed. Protein, polysaccharides and humic acid are used as models for biomolecules.

2. Experimental

2.1. Materials

PES UF membrane with nominal molecular weight cut-off (NMWCO) of 100 kg/mol (kDa) from Sartorius, Germany (SG-100) was used as the base membrane for post-modification via photo-grafting. In addition, PES UF with NMWCO of 10 kg/mol was used for the performance comparison. To avoid the effects of initial property variation, only membrane having initial water permeability in the range ± 15% relative to the average values were used for the experiments. Poly(ethylene glycol) methacrylate (PEGMA 400, the number indicating molar mass in g/mol) from Polysciences Inc., Warrington, USA was used as the functional monomers. N,N′-methylene bisacrylamide (MBAA) as cross-linker monomer and myoglobin from horse skeletal muscle (95–100% purity), were purchased from Sigma-Aldrich. Myoglobin solution (in phosphate buffer pH 7) was pre-filtered through a 0.45 μm microfilter (Sartorius, Germany) to remove undissolved material. Commercial PES polymer (Ultrason E 6020 P) from BASF (Ludwigshafen, Germany) was used and dried at 120 °C for at least 4 h before use. N-methyl-2-pyrrolidone (NMP) was purchased from Merck. Polyvinylpyrrolidone (PVP) (MW ~10.000 g/mol) and dextran were purchased from Serva Feinbiochemica GmbH&Co (Heidelberg, Germany). Polyethylene glycol (PEG), potassium dihydrogen phosphate (KH_2PO_4) and disodium hydrogen phosphate dihydrate ($Na_2HPO_4.2H_2O$) were purchased from Fluka. Bovine serum albumin (BSA) was purchased from ICN Biomedicals, Inc. (California, US). Humic acid (HA) as model of phenolic compound was purchased from Sigma-Aldrich.

2.2. Methods

2.2.1. Membrane hydrophilization by post-modification via photo-grafting

The method and experimental set-up used for this modification have already been described in previously reported literature [17]. Briefly, a UVA Print system (Hoenle AG, Gräfelfing, Germany) equipped with a high-pressure mercury lamp, emitting wavelengths >300 nm and providing homogenous illumination of up to 100 cm^2 area with an intensity of 35 ± 5 mW/cm^2, was used. PES membrane samples were immersed into monomer solutions in a Petri dish and then subjected to UV irradiation for various time periods. After modification, the membranes were rinsed and washed with water, respectively. Degree of grafting (DG) was used to quantify the amount of grafted polymer on the membrane surface, which was determined by the following equation:

$$DG = \frac{m_m - m_o}{A} \quad (1)$$

where m_o is the initial membrane sample weight, m_m is the membrane weight after modification and A is the outer surface area of the membrane used. Control experiments for the washing process as well as gravimetric method were also performed.

2.2.2. Membrane hydrophilization by polymer blend during phase separation

The method for the membrane preparation has been reported in our previos publication [5]. PES with certain concentration and PEG as hydrophilic agent to were dissolved in NMP until the homogenous solution was obtained. Polymer solution without an additive was also prepared for the control experiments. The homogenous polymer solution was left without stirring until no bubble was observed and the membranes were prepared by using home-made casting machine. The polymer solution was cast with a thickness of 200 μm using a steel casting knife on a glass substrate (casting speed ~80 mm/s). Thereafter, the proto-membrane was solidified in a coagulation bath containing water (25 °C ± 2) for 1 h. The resulting membranes were washed and soaked in water for 24 h before drying.

2.2.3. Membrane hydrophilization by reactive phase separation

PES was dissolved in N-methyl-2-pyrrolidone, and polymeric additive was added to the polymer solution. The polymer solution was cast on a glass substrate and subjected to UV light (Switzerland). Thereby, it was expected that the hydrophilic polymer additive will covalently be attached to the membrane matrix polymer in a single process. Thereafter, the proto-membrane was solidified in a coagulation bath containing water for 1 h. The resulting membranes were washed and soaked in the water for at least 24 h before drying.

2.2.4. Membrane characterization

The membrane characterization included surface chemistry, surface hydrophilicity and surface morphology. The membrane surface chemistry was observed by using the Varian 3100 Fourier transform infrared spectroscopy (FTIR) Excalibur series. A total of 64 scans were performed at a resolution of 4 cm^{-1} and the temperature of 21 + 1 °C.

The surface hydrophilicity was observed by measuring the contact angle. Sessile drops static contact angle (CA) was measured using an optical contact angle measurement system (OCA 15 Plus; Dataphysics GmbH, Filderstadt, Germany). Five microlitres of water was dropped on the membrane surface from a microspyringe with a stainless steel needle in room temperature (21 ± 1 °C). At least five measurements of drops at five (at least) different locations were averaged to obtain CA for one membrane sample.

The top surface morphology of the membrane was observed by using a Quanta 400 FEG (FEI) environmental scanning electron microscope (ESEM) at standard high-vacuum conditions. Before measurement, the

outer surface of membrane sample was coated with gold/palladium (0.5 min).

2.2.5. Procedures for adsorptive fouling resistance evaluation and ultrafiltration

All experiments were carried out by using a dead-end stirred cell filtration system (Amicon cell model 8010 for adsorptive fouling measurement, model 8050 for UF experiments) connected to a reservoir (~500 mL) and pressurized by nitrogen from a gas tank. In all experiments, membrane compaction was firstly performed by filtration of pure water at 450 kPa for at least 0.5 h. For static adsorption experiments (adsorptive fouling), a biomolecule model solution was added to the cell and the outer membrane surface was exposed for 3 h without any flux at a stirring rate of 300 rpm. Afterwards, the solution was removed, and the membrane surface was rinsed two times by filling the cell with pure water (5 mL) and shaking it for 30 s. Water fluxes before and after exposure were measured at the same pressure (300 kPa). The evaluation of adsorptive fouling resistance was expressed in terms of relative flux reduction (RFR) determined by the following equations:

$$RFR = \frac{J_0 - J_a}{J_0} x100\% \quad (2)$$

where J_o and J_a are water flux before and after exposing to the biomolecule model solution test, respectively.

Ultrafiltration experiments at a constant trans-membrane pressure were conducted using a biomolecule solution as the feed. The permeate flux profile over time of filtration was investigated. The UF performance was expressed in terms of permeate flux to initial water flux ratio. Myoglobin, BSA and HA concentrations were determined by measuring their UV absorbances, whereas dextran concentration was measured by gel permeation chromatography. The apparent biomolecule rejection was calculated by using the following equation:

$$R = 1 - \frac{C_{downstream}}{C_{upstream}} \quad (3)$$

3. Results

3.1. Hydrophilization of UF membranes by post-modification via photografting

To verify if the modification has taken place, the surface chemistry of the membranes before and after modification was analyzed using FTIR. Fig. 1 shows an example of IR spectra for unmodified and

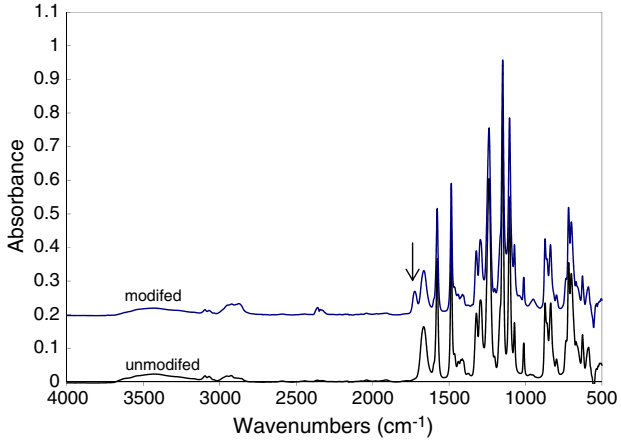


Fig. 1. ATR–IR spectra of unmodified and PEGMA-modified PES membranes.

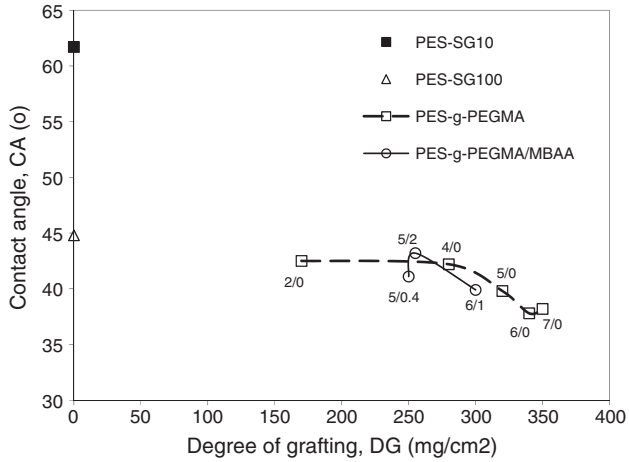


Fig. 2. Contact angles of unmodified and modified membranes with monomer concentration of 40 g/L at various DGs. The numbers inside the picture indicate the UV irradiation time (for single number) and UV irradiation time and cross-linker concentration (g/L), respectively (for number couples).

PEGMA-modified PES membranes. It is seen that, observable changes in IR spectra were identified after modification. Additional peak in the IR spectrum was identified through the appearance of C = O vibration from the ester group of methacrylate at ~1725 cm^{-1}.

As presented in Fig. 2, the hydrophilicity of the membrane surface was increased by the modification. PEGMA-modified membranes had CA ranging from 37.8 ± 4.2° to 42.5 ± 4.3° depending on the degree of grafting (DG). The increase in DG increased the membrane hydrophilicity as indicated by decreasing contact angle. These values are somewhat smaller than the unmodified base membrane (44.8 ± 4.2°), but much lower than for the unmodified membrane (PES-SG10) having similar nominal cut-off (61.7 ± 2.5°). A systematic change in CA caused by degree of grafting indicates that the difference in CA is due to the modification and is not due to data deviation. These CA results agree well with previously reported CA of PEGMA-modified PAN membranes [18].

Further experiments were done by using PES-PEGMA-modified membranes with the DG within the range 310 to 325 μg/cm^2 (Hydraulic permeability 1.2–1.5 L/m^2hkPa, cut-off ~10 kDa) and PES-PEGMA/MBAA membranes with the DG within the range 105 to 115 μg/cm^2 (0.75–0.85 L/m^2hkPa, cut-off ~0.8 kDa). These DG values resulted in optimum characteristics considering CA and hydraulic permeability data.

Fig. 3 shows the adsorptive fouling resistance of the unmodified and modified membranes using several biomelecule model solutions.

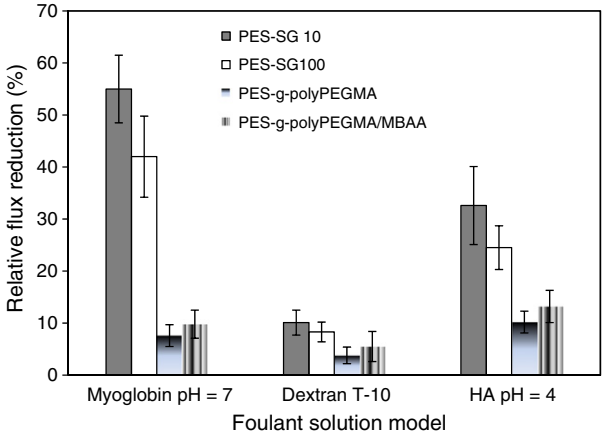


Fig. 3. Relative flux reduction of unmodified and modified membranes after adsorptive fouling experiments using different biomolecules models solution.

It is seen that the flux reduction of modified membranes were smaller than unmodified membranes for all biomolecule models.

Fig. 4 shows the UF experiment results. Interestingly, all modified membranes had much higher flux ratio than both unmodified membranes. During UF of myoglobin solution (top panel), the unmodified membranes had stable permeate flux of only ~20% (for PES-SG 100) and ~30% (for PES-SG10) relative to initial water flux, whereas modified membranes had more than 80%. A common phenomenon during fouling study was also observed in this work, i.e. membrane with larger pore size leading to high flux yielded more severe fouling (higher flux loss relative to the initial water flux) than membrane with smaller pore size (cf. PES-SG10 and PES-SG100) even though it had smaller flux loss in the beginning of operation. All modified membranes had slightly lower protein rejection than PES-SG10 unmodified membrane (70% for the unmodified and 60% for the modified membranes). Similar phenomena were observed for ultrafiltration of dextran and humic acid solutions.

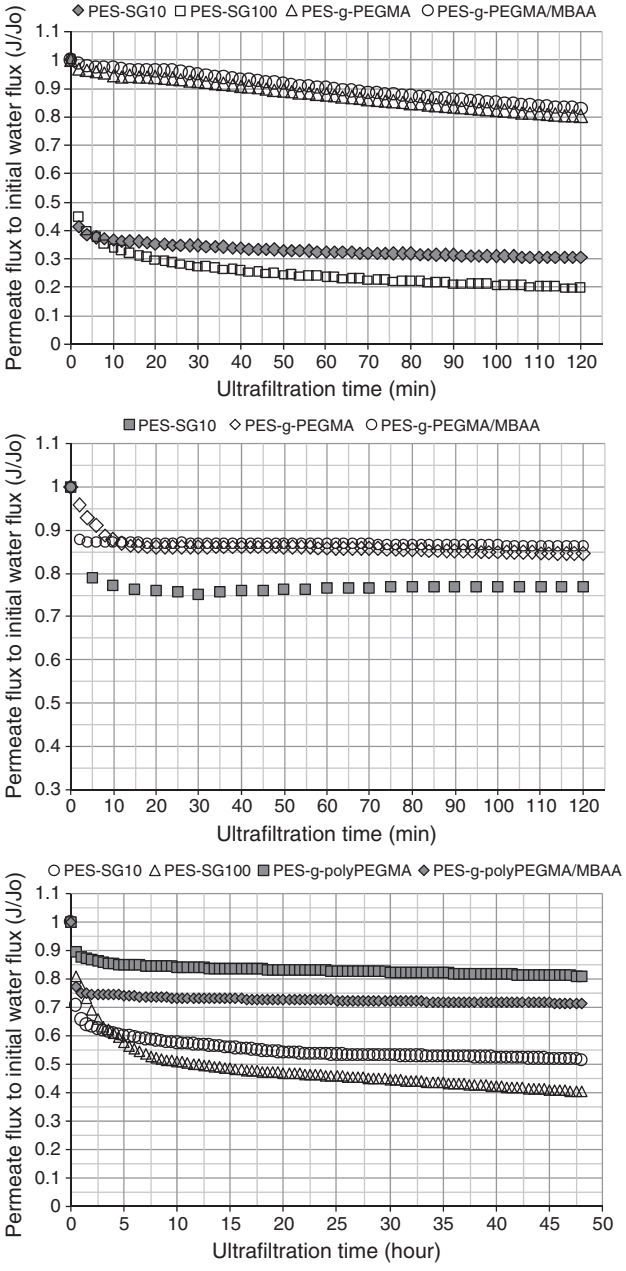


Fig. 4. Flux ratio profile as a function of time during ultrafiltration of 1 g/L myoglobin solution (top panel), of 1 g/L of dextran T-10 solution (middle panel) and of 50 mg/L (pH 7.2, 1 mM Ca^{++}, conductivity 1100 μS/cm) humic acid solution (bottom panel).

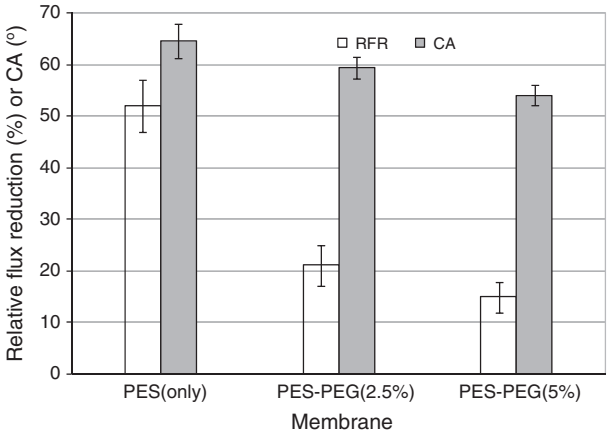


Fig. 5. Relative flux reduction after static adsorption using BSA (1 g/L in phosphate buffer 0.05 M, pH 7, 3 h exposure) and the membrane contact angle (CA). The error bars represent standard deviation.

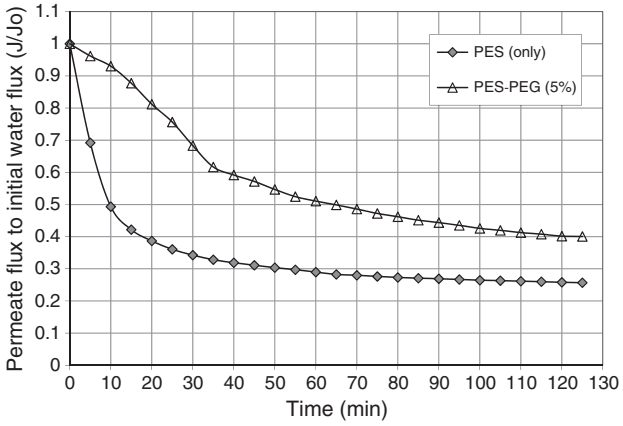


Fig. 6. Normalized flux during ultrafiltration of BSA solutions (0.1 g/L in phosphate buffer 0.05 M, pH 7) at a trans-membrane pressure of 300 kPa.

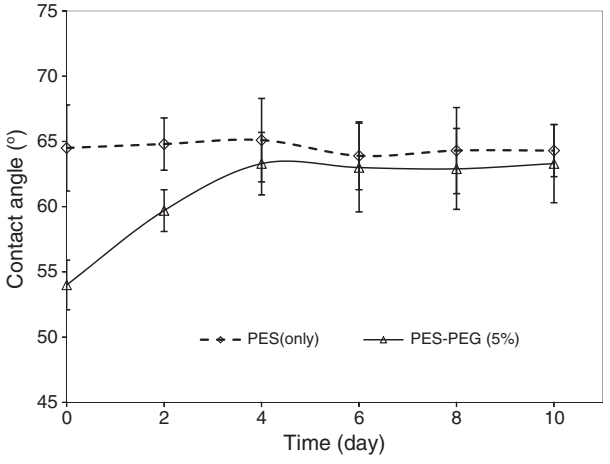


Fig. 7. Stability examination of modifier agent in polymeric membrane investigated by measuring the contact angle as a function of incubating time. The membranes were soaked in water 40 °C.

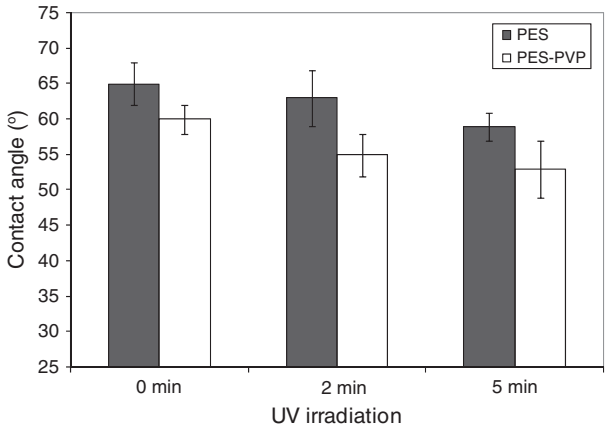


Fig. 8. Effect of PVP and UV irradiation on the membrane contact angle. The PES and PVP concetration were 13% and 5% w/w, respectively.

3.2. Membrane hydrophilization by polymer blend during phase separation

In this work, membrane hydrophilization was performed by blending of hydrophilic modifier agent (here is PEG) and polymer membrane during membrane preparation via phase separation (PS). As clearly seen in Fig. 5, the membranes prepared with an addition of hydrophilic modifier showed significantly higher resistance towards adsorptive fouling than the membrane prepared without addition as noticed by their much lower RFR. As the concentration of PEG was increased the RFR would decrease. In addition, it is obviously seen that the addition of PEG increased the membrane hydrophilicity. Addition of PEG 5% decreased the membrane CA from 65° to 54°. The more PEG was added, the more hydrophilic membrane was resulted.

Fig. 6 shows the ultrafiltration experiment results. As also observed in the previous section, it was observed that permeate flux dropped rapidly in the beginning of filtration for both membranes. Indeed, the presence of hydrophilic macromolecular additive increased the permeate flux. The membrane prepared without an additive had stable permeate flux of only ~25% relative to the initial water flux, whereas the PES-PEG membrane had higher permeate flux (40%). It should be noted that both membranes had similar cut-off (~1.5 and ~1.4 kDa for PES (only) and PES-PEG membranes, respectively). Nevertheless, stability experiments indicated that PEG could leach out from the membrane matrix after certain time (Fig. 7). The membrane contact angle increased with increasing the soaking time in water (40 °C).

3.3. Membrane hydrophilization via reactive phase separation

To increase the stability of modifier agent in membrane matrix, the proto-membrane after casting was exposed to the UV irradiation. First, PVP was used as the macromolecular additive because PVP is one of the most well-known hydrophilic additives during manufacturing of flat-sheet or hollow-fiber membranes from PSf or PES [19]. Fig. 8 shows the effect of UV irradiation on the membrane contact angle for the membranes prepared with and without addition of PVP.

It is clearly seen that all membranes prepared with addition of PVP have lower contact angle than the membranes prepared without PVP. Further, for the membrane prepared with PVP, the effect of UV irradiation on membrane hydrophilization was also observed. As the UV irradiation was increased the membrane CA decreases. A new significant peak at 1678 cm^{-1} assigned to a primary amide stretch was observed for the membrane prepared with addition of PVP. No difference in FTIR data was observed for the membrane prepared with addition of PVP with and without UV irradiation. Overall, similar results were found from the experiment using PEG as additive. However, as also found in the conventional PS no new peak was observed for the membrane prepared with addition of PEG.

Fig. 9 shows the surface morphology of the membrane surface for different membrane. It is observed that all membranes have pore sizes within the nanometer range. Comparing the PES membranes prepared

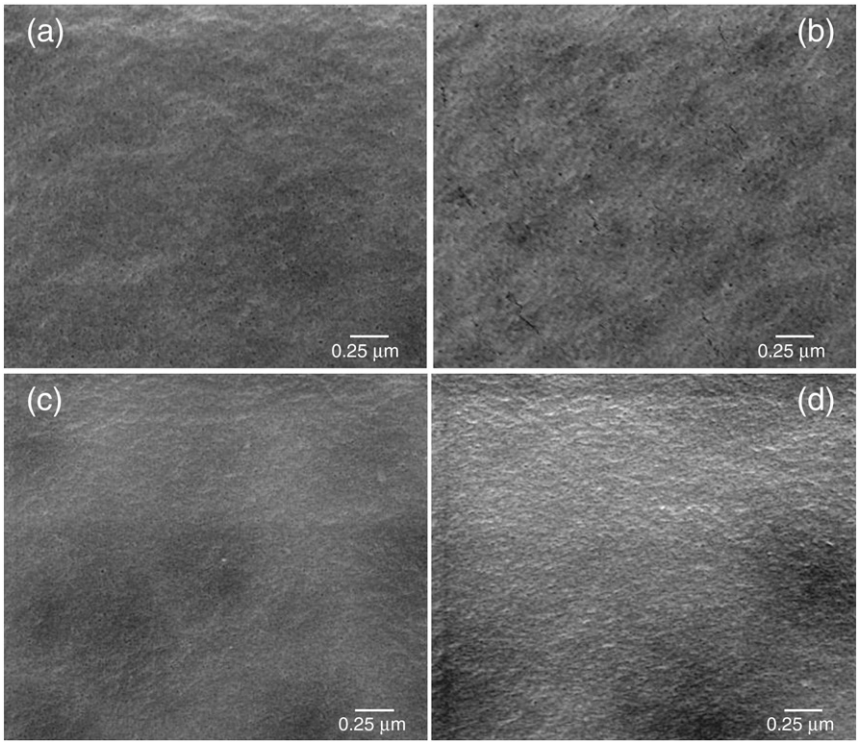


Fig. 9. Surface morphology of the membrane: (a) PES without UV irradiation, (b) PES with 2 min UV irradiation, (c) PES-PVP without UV irradiation and (d) PES-PVP with 2 min UV irradiation.

with no PVP without (Fig. 9 (a)) and with (Fig. 9 (b)) UV irradiation it is observed that both membranes have significant difference in pore size. The addition of PVP into polymer solution resulted in membrane having smaller pore size than without addition of PVP (Fig. 9 (a)) and with (Fig. 9 (c)).

Fig. 10 shows the flux reduction after adsorptive fouling experiment using BSA solution. It is clearly seen that addition of PVP could increase the resistance towards adsorptive fouling. Furthermore, the UV irradiation increased the fouling resistance for both PES and PES-PVP membranes. For all membranes, the RFR after exposing to BSA solution pH 8 were lower than pH 5.

Ultrafiltration results are presented in Fig. 11. In principle, similar result with previous section was obtained, i.e., flux decline in the beginning of filtration was observed. Membrane prepared with addition of hydrophilic modifier had higher resistance towards fouling than without additive. Interestingly, PES-PVP membrane with UV irradiation had higher flux for long term application even though it had lower flux in the beginning of filtration.

In order to know the stability of the hydrophilic additive in the membrane matrix, the PES-PVP and PES-PVP-UV were soaked in water (40 °C) and sodium hydroxide (0.01 N). CA was used as the indicator for the stability. Changes in CA are smaller for UV-irradiated membranes (Fig. 12). Initially, both membranes had the similar contact angle. After 10 days soaking in water the membrane prepared with UV irradiation had smaller CA. Similar trend is observed when NaOH solution is used instead of water for soaking medium. The stability test identified via observation of IR absorbance shows similar results.

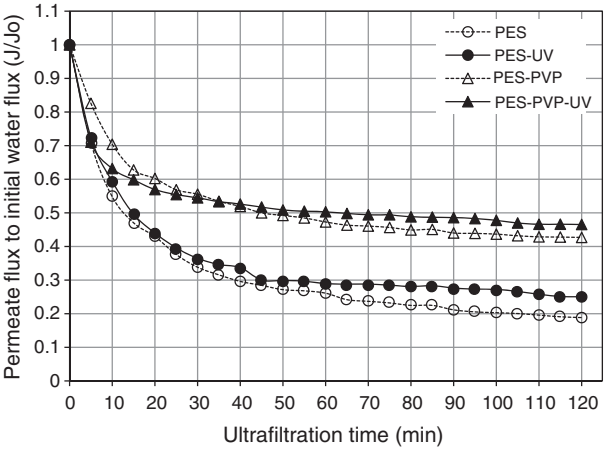


Fig. 11. Flux profile during ultrafiltration of BSA solutions (0.1 g/L in phosphate buffer 0.05 M, pH 5) at a trans-membrane pressure of 300 kPa.

4. Discussion

4.1. Membrane characterization

Membrane characterization data confirm that all hydrophilization methods (post-modification via photo-grafting, conventional polymer blend during NIPS and reactive NIPS) changed the membrane characteristics. New peak in IR spectra confirms that the hydrophilization changes the membrane surface chemistry. Although no additional peak was observed after hydrophilization using PEG in conventional NIPS (the reason for this result would be overlapping bands of the strongest bands for PEG (ether) with bands for PES (ether)), but significant increase in intensity of C—O at ~1105 cm^{-1} confirms the presence of the additives in the polymer membrane matrix. All hydrophilized membranes had lower contact angle indicating more hydrophilic than unmodified membranes having similar cut-off. Increasing membrane hydrophilicity was influenced by DG (for photo-graft modification), modifier agent concentration (for conventional NIPS) and modifier agent concentration and UV irradiation (for reactive NIPS). Nevertheless, care should be taken to interpret CA data. The CA of the membrane is affected by the membrane material (chemistry), amount and structure of the modified agent and pore structure [17]. Hydrophilization via photo-grafting could narrow and even block the pores of the base membrane as evidenced by significant smaller water

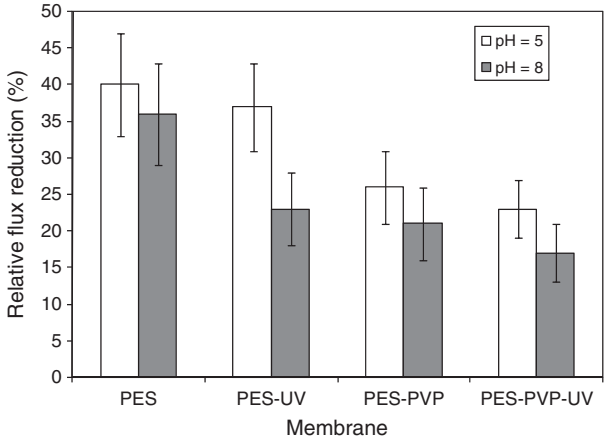


Fig. 10. Relative flux reduction after adsorptive fouling experiments using BSA solution (1 g/L in 0.05 M phosphate buffer, 3 h exposure). The error bars represent standard deviation.

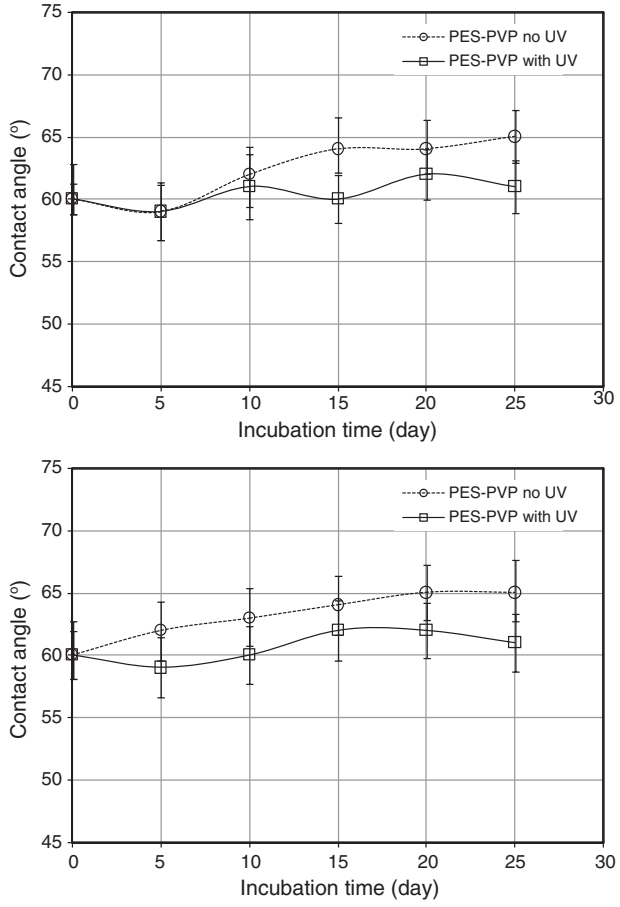


Fig. 12. Stability examination of modifier agent in polymeric membrane investigated by measuring the contact angle as a function of incubating time. The membranes were soaked in water 40 °C (top panel) and 0.01 N NaOH (bottom panel).

flux after hydrophilization. On the other hand, the hydrophilic character of the membrane prepared by conventional PS was not stable as indicated by decreasing CA with increasing incubating time (Fig. 7).

SEM images (Fig. 9), CA and FTIR data suggest that reactive phase separation performed by exposing the proto-membrane to UV irradiation after casting (before coagulation) could also be used for a novel hydrophilizatrion. Changing in surface morphology of the PES membrane after UV irradiation indicates that the PES is intrinsically sensitive to UV irradiation (note that no photo-initiator was added in this experiment). This observation supports the CA data, where the PES membranes prepared without addition of PVP showed smaller contact angle for the membrane prepared with application UV irradiation. For the same material, the larger pore size the smaller contact angle. Interestingly, Fig. 9 (d) indicates that the addition of PVP could suppress the effect of degradation by UV light. In addition, the indication of new material appears more significant in the presence of UV irradiation. Interestingly, membrane having stable hydrophilic character was resulted from reactive NIPS method. This could be seen from the CA and FTIR data showing that no change in both characteristics was observed after incubating in water in sodium chlorite. Thus, the UV irradiation increased the stability of PVP in polymer membranes.

4.2. Fouling behavior

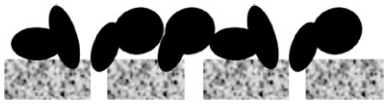
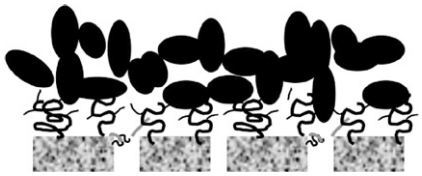
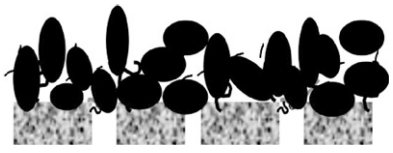
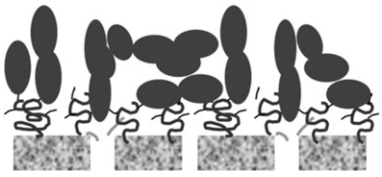
In all experiments, it was observed that the water flux after adsorptive fouling was smaller than before exposing to the biomolecule model solution. This phenomenon suggests that there was biomolecule binding to the membranes due to adsorption process. The relative flux reduction data indicate that protein was the strongest foulant (as indicated by their highest flux reduction), whereas dextran (polysaccharide) was the weakest foulant among biomolecule models. Beside the membrane characteristics, the feed solution characteristic influences clearly the extent of fouling. Protein solution having negatively charge (here BSA pH 8) resulted in lower adsorptive fouling than protein solution having neutral overall net charge (here BSA pH 5). The effect of pore size on fouling was also observed (cf. Ref [17,20,21] for detail explanation).

In all UF experiments, it was observed that permeate flux dropped rapidly in the beginning of filtration followed by gradually decreased to relative constant flux. On the one hand, this phenomenon indicates that concentration polarization has taken place. On the other hand, the difference in flux profile for different membranes suggests that fouling also contributed to the permeate flux decline (note that the membranes had similar pore size). In addition, this observation is supported by the experimental results, which showed that stopping the filtration experiment for 5 min and then restarting could not reach the initial flux. Furthermore, external cleaning could increase the water flux (compared to the ultrafiltration flux) but it was still lower than initial water flux. Ultrafiltration using the membranes prepared by reactive PS showed that in the beginning of UF no significant difference was observed between the membranes with and without irradiation. However, after one hour filtration PES-PVP membrane with UV irradiation starts having higher flux than PES-PVP membrane without irradiation. This may indicate that the PVP at the membrane without irradiation starts leaching out from the membrane matrix and the membrane becomes more hydrophobic leading to higher fouling. This explanation is supported by the stability test data, which shows that increasing CA was found after 10 days incubation in both water and alkaline solution (Fig. 7).

4.3. Effect of membrane hydrophilization on membrane characteristics and fouling behavior

Fouling resistance examination showed that modification was successful to increase the resistance towards both adsorptive fouling and ultrafiltration fouling. The higher fouling resistance of the modified membranes can be explained by the presence of hydrophilic modifier in/on the membrane. To more specific, the increase in fouling resistance

Table 1
Illustration of hydrophilic structure for different hydrophilization methods and their corresponding characteristic and their fouling description.

No.	Membrane hydrophilization method	Solute/particle deposition		Property
		Short term application	Long term application	
1.	Conventional phase separation without modification			High fouling
2.	Photo-grafting (post-modification)			- Low fouling - Stable modification - Flux decreases due to modification
3.	Blending modification phase separation			- Low fouling in the beginning - Low modification stability - Flux decreases or increases due to modification
4.	Reactive phase separation			- Low fouling - Stable modification - Flux decreases or increases due to modification

for the membrane prepared by photo-graft copolymerization has been well explained in previous publications [17,22,23].

Membrane post-modification can increase the resistance towards fouling. However, due to pore narrowing (even blocking) by modifier polymer, decreasing hydraulic permeability (data not shown) could not be avoided. Certainly, this effect should be minimized. Further, additional step is needed after membrane preparation via PS. Blending modifier agent and polymer membrane during PS as simple method showed significantly higher resistance towards fouling than the membrane prepared without an additive. Nevertheless, stability experiments showed that modifier agent could leach out from the membrane matrix after certain time.

Synergistic effect between addition of PVP and UV irradiation seemed to occur during hydrophilization. For the PES membrane, polymer degradation caused both pore enlargement (from the permeability measurement as well as SEM data) and increase in the (negative) surface charge of the membrane (ZP at pH 4 and pH 8 for PES without UV irradiation are −5.2 and −35.9 mV; respectively whereas ZP at pH 4 and pH 8 for PES-UV are −14.9 and −37.8 mV; respectively). Therefore, the flux reduction after exposing to BSA pH 8 was smaller than pH 5. It should be noted that at pH 8 the BSA solution should have negative charge. Thus electrostatic repulsion between protein and membrane should take place leading to smaller flux reduction. Comparing the PES and PES-PVP membranes with and without UV irradiation shows that the difference in flux reduction between PES and PES-UV membranes is larger than between PES-PVP and PES-PVP-UV membranes. This phenomenon indicates that the resistance towards fouling is influenced not only by charge interaction but also by hydrophilization. Further, the slight difference in flux reduction between PES-PVP membranes for both pHs suggests that the effect of hydrophilization is more dominant than charge effect. In general, Table 1 summarizes the advantage and disadvantages of hydrophilization method as well as their corresponding characteristic and fouling description.

5. Conclusions

Three different approaches for preparing polymeric low fouling UF membranes have been described. In conventional phase separation without hydrophilization, membrane–solute/particle interaction is high due to hydrophobic nature of the PES membrane. This condition yields solute adsorption followed by solute deposition on the membrane surface. For the long term application, the deposition will be more significant due to the contribution of solute–solute interactions. Membrane–solute interaction could significantly be reduced by hydrophilization via post-modification. As consequence, less solute/particle deposition is obtained. This phenomenon was found for both short and long term applications. However, flux reduction after post-modification was identified as disadvantage of this modification method. Further, from practical point of view, this method needs addition step after membrane preparation. The hydrophilization by blending polymer membrane with hydrophilic agent during PS resulted in membranes having low interaction with solute/particle. Nevertheless, for long term application the membrane–solute interaction becomes more pronounced due to leaching out of hydrophilic agent from polymer membrane. The membrane prepared by reactive PS had low interaction with solute/particle for both short and long term application. Reactive PS performed by integration of UV irradiation into conventional PS seemed to combine the advantages of those both methods. The stability of the membrane could be increased and the modification could be done in one step process.

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